

Systematics in the metal-insulator transition temperatures in vanadium oxides

B. Fisher, J. Genossar and G. M. Reisner

Physics Department, Technion, Haifa 32000, Israel

Abstract

Nine of the known vanadium oxides, $\text{VO}_{2-1/n}$ (n - a positive or negative integer) with $n=2, 6, 8, 9, \infty$ and -6 , undergo metal-insulator transitions accompanied by structural transitions, at various temperatures T_{MIT} (V_7O_{13} is metallic above $T=0$). Among the persistent efforts to determine the driving force(s) of these transitions, electron-electron (Mott-like) and electron-phonon (Peierls-like) interactions, there were several attempts to find systematics in T_{MIT} as function of n . Here we present an unexpectedly simple and illuminating systematics that holds for positive n : if T_{MIT} is the absolute value of the difference between $T_M(n)$ and $T_P(n)$, which represent the contributions of electron-electron and electron-phonon interactions, respectively, all data points of $T_M - T_P$ versus $1/n$ lie on, or close to, two simple straight lines; one is $T_M - T_P = T_\infty(7/n - 1)$ for V_3O_5 , V_4O_7 , V_5O_9 , V_7O_{13} , V_8O_{15} , V_9O_{17} and VO_2 and the other is $T_M - T_P = T_\infty(3/n - 1)$ for V_2O_3 , V_6O_{11} and VO_2 .

Keywords:

A metal - semiconductor, D electron-electron interactions, D electron-phonon interactions, D phase transitions

1. Introduction

The general formula $\text{VO}_{2-1/n}$ (n - a positive or negative integer) represents all known vanadium oxides. The monovalent members of the family with $n=1$ (VO) and $n=-2$ (V_2O_5) are metallic and semiconducting at all temperatures, respectively. The monovalent oxides with $n=2$ (V_2O_3) and $n=\infty$ (VO_2) and the mixed valent oxides with $n=3 - 6, 8, 9$ and -6 , undergo metal-insulator transitions (MIT) accompanied by structural transitions, at various temperatures, T_{MIT} , below and above room temperature. The mixed valence compounds with positive n belong to the so-called Magneli phases and those with negative n - to Wadsley phases. These transitions, including the absence of a transition for $n=7$, have attracted attention over many decades. One of the subjects under debate for more than half a century, was the role of the electron-electron (Mott-like) and electron-phonon (Peierls-like) interactions in these transitions [1, 2, 3]. Along with the efforts to understand the nature of these phase transitions there have been several attempts to find a systematic behavior of T_{MIT} as function of n . In 1971, when only the T_{MIT} of the Magneli phases with $n=4 - 8$ were known, Nagasawa showed that (1) Magneli phases are classified into two groups by the transition temperatures in which one has even n and the other odd n and (2) transition temperatures decrease with the increase of even and odd n (the line for the two odd n lies below that connecting the three for even n). In 1980 [5], using data from References [6, 7] for $n < 8$ we showed that T_{MIT} plotted versus $1/n$ lie on, or close to several straight lines as shown below:

(a) $T_{MIT} = T_{MIT}(\infty)(1 - 1/n)$ for $n = 1, 2, 4$ and ∞ ,

(b) $T_{MIT} = T_{MIT}(\infty)(1 - 3/n)$ for $n = 5, 6$ and ∞ ,

(c) $T_{MIT} = T_{MIT}(\infty)(7/n - 1)$ for $n = 3, 4, 5$ and 7 .

where $T_{MIT}(\infty) = T_{MIT}(\text{VO}_2)$. Note that the lines (a) and (c) cross at $1/n = 1/4$ and that the lines (a) and (b) meet at $1/n = 0$. The then available data hinted at the existence of another simple line, (d) $T_{MIT} = T_{MIT}(\infty)(1 - 7/n)$ (the reflection of (c) about the vertical axis $1/n = 1/7$) for $n = 7, 8$ and ∞ , but the discrepancy of the data point for $n=8$ was far too large in view of the close agreement of the

points in (a) - (c). At that time, the metallic nature of VO was still problematic, its non-metallic conductivity being governed by the large concentration of native defects. In 2007 experimental and computational evidences were presented in support of VO being a strongly correlated metal [8]. The attempt to include the solitary data point with negative n ($n=-6$) in the systematics is ignored here.

The renewed inspection of the systematics was motivated by later reports in the literature, including $T_{MIT}(V_9O_{17})$ [9, 10, 2] which strengthened confidence in the previously reported systematics. Two questions were asked at this stage: 1. How valid are these simple lines? 2. If they are valid, what do they imply?

In order to answer the first question, a wide spread of $T_{MIT}(x)$ data, where $x=2-1/n$, obtained over the years by many groups from electrical and magnetic measurements were tabulated and plotted; these data include thermal hysteresis and experimental errors. Appendix A is devoted to the verification of these lines.

The so proven validity of the data used in References [1], [2] and [5] and the present understanding in the field allowed a revision of the interpretation of T_{MIT} that simplified the systematics to being expressed by only two straight lines.

2. Transition temperatures of VO_x

The transition temperatures of the vanadium oxides shown in Table I were taken mainly from Reference [6]; the data missing in that early article were filled in from more recent publications. Graphs of $T_{MIT}(x)$ using data from this Table appear in research articles and reviews related to VO_x such as [1, 11, 2]. A similar graph including also the datum for V_9O_{17} as in [2], is shown in Fig. 1 where the primary and secondary horizontal axes have been extended to $x=1$ and $n=1$. Solid lines connect the data points as in the above references. The four dashed straight lines which in part overlap with the solid lines represent (a) - (d), their expressions shown in the previous section. The datum for V_9O_{17} was available in 1981 but was ignored in literature until 2013. As in [5], the point for V_8O_{15} deviates significantly from line (d) and that for V_3O_5 deviates

slightly from line (c) (430 K instead of 453 K).

The most interesting pair of lines in Fig. 1 is of course the (c) - (d) pair, for which $T_{MIT} = \pm 340(7/n-1)K$; these two lines contain most of the data points for T_{MIT} from $n=3$ to $n=\infty$. Thus, *if the line representing $T_{MIT} = 340(1-7/n)K$ and the points laying on it (including that for $n=8$) are rotated around the horizontal axis, all the points of the (c) - (d) pair lie now on a single straight line with the point for $n=8$ close to it.* This simple transformation leaves out two points on what previously was line (a) ($1/n=1/2$ and 1) and one point on the former line (b) ($n=1/6$). If the point for $n=1/6$ is reflected about the horizontal axis we obtain a new straight line that connects the points for $1/n=1/2$, $1/n=1/6$ and $1/n=0$. It turns out that the ordinate of the new graph represents the difference between two functions, while that of the old graph represents the absolute value of this difference. And indeed, the zero for V_7O_{13} is not a minimum but a crossover point. The most suitable names for the two functions are T_M and T_P (M for Mott and P for Peierls). The data points in Fig. 2 represent $T_M - T_P$ versus $1/n$ for all V_nO_{2n-1} with $n>1$; the solid lines are the fitted linear trendlines with their Patterson correlation coefficients. The dashed lines represent the ideal relations $T_M - T_P = 340(7/n - 1)K$ and $T_M - T_P = 340(3/n-1)K$. The upper dashed line is distinguishable but still very close to the solid line. The lower dashed line is indistinguishable on the scale of Fig. 2, it overlaps the corresponding solid line. The point for $n=1$ (VO) remains isolated; the extrapolation of line (a) in Fig. 1 to 0 for $n=1$ is not understood.

3. Discussion

The discussion on the MIT in V_nO_{2n-1} is based on essentials of the state of the art of this topic as described in References [1] and [2]. The rutile VO_2 structure contains pairs of translationally distinct but symmetry equivalent, parallel, infinite chains of edge sharing octahedra. In V_nO_{2n-1} the chains are broken into n -octahedra long units; the symmetry is broken in such a way that rutile-like chain fragments are connected by corundum - like (V_2O_3 -like) chain ends.

The two parallel chains become symmetry inequivalent and are denoted in [2] as "A" and "B". Theoretical calculations for several V_nO_{2n-1} compounds [1] showed that electron-lattice interactions are largest in the centers of the chain-fragments while electron-electron interactions are largest at the fragments' ends. Recent experiments [12] confirm the importance of electron-electron correlations in V_3O_5 (the highest point of Fig. 2). With increasing n the electron-lattice interaction increases while the electron-electron interaction decreases. The absence of transition in V_7O_{13} is probably due to mutual cancelation. For V_2O_3 $T_M > T_P$; this is not surprising since this material was originally considered a canonical Mott system. The location of VO_2 at the bottom of Fig. 2 is also not surprising; the structural ordering and pairing at low temperatures imply a dominant Peierls instability.

The initial systematics presented in the Introduction consisted of the three straight lines (a) - (c) and hinted at line (d) symmetrical to (c). The updated point for V_9O_{17} validated line (d) and enabled reduction to two lines to represent the systematics of $T_{MIT}(1/n)$. The splitting into two lines occurs between V_2O_3 and $V_3O_5=V_2O_3+VO_2$. $T_{MIT}(V_3O_5)$ and $(T_M - T_P)(V_3O_5)$ are much higher than those of the constituents. We suggest that this is due to the presence of interfaces between V_2O_3 and VO_2 . There are now many examples in the literature showing that the properties of double-, or multi-layers deviate strongly from those of the constituents due to the interface(s). Once the interfaces between V_2O_3 and VO_2 are formed, the addition of rutile fragments allows for a monotonic (linear) variation of $(T_M - T_P)(1/n)$.

Rather surprising is the location of the point for V_6O_{11} : why should the point for this compound "leave its neighbors" and "join" instead the straight line connecting V_5O_9 to VO_2 in Fig. 1 and then fit exactly on the line connecting V_2O_3 to VO_2 in Fig. 2? A hint is provided by the very different dependencies on n of the a and b parameters (of chains A and B) as shown in Fig. 6 of Ref. [2]. Above $n=3$, in both the strong and weak electron-electron interaction regimes a decreases monotonically with increasing $x=2-1/n$; the accompanying behavior of b is at first a weak and then an accelerated decrease until $x=1.83$

is reached; above this point b increases linearly with x towards $x=2$ (for VO_2); a V-shaped $a(x)$ feature is formed with the tip at $n=6$ ($x=1.83$). Electronic structure calculations [1] show that electron-electron interactions are stronger in the B chain leading to localization that inhibits electron-lattice coupling. It is possible that the sudden jump of the data point for V_6O_{11} out of the upper line in Fig. 2 is correlated with the structural anomaly of $b(x)$; however the exact fit to the lower line is puzzling and requires a stronger argument. If indeed the jump of the data point for V_3O_5 above that for V_2O_3 is due to an interface effect, the question now is why does this effect disappear completely in the case of V_6O_{11} ?

4. Summary

The systematics of T_{MIT} of $\text{VO}_{2-1/n}$ as function of n for $1 \leq n \leq \infty$ proposed in 1980 [5] is revisited here. The renewed interest was motivated by a crucial datum that was not available at that time and by the advances in the understanding of the MIT in this family of oxides. These lead to a simplified systematics expressed by two simple expressions; one is $T_M - T_P = T_\infty(7/n-1)$ for V_3O_5 , V_4O_7 , V_5O_9 , V_7O_{13} , V_8O_{15} , V_9O_{17} and VO_2 and the other is $T_M - T_P = T_\infty(3/n-1)$ for V_2O_3 , V_6O_{11} and VO_2 where T_{MIT} is the absolute value of $T_M - T_P$. These two expressions emphasize the smooth transition from a Mott-like to a Peierls-like regime of the MIT in this family of materials. The linearity of the difference of the two functions in $1/n$, and the existence of two lines, not one, are very intriguing and should be derived from theoretical calculations.

5. Appendix A

Most data used in [5, 1, 11, 2] are based on Table II (magnetic measurements) of [6] while data in Table I of that report (electrical measurements) include thermal hysteresis. Measurements of T_{MIT} of the vanadium oxides have been carried out by many groups. Their data are represented in some cases by a single number, but in most cases by a range of temperatures which include

thermal hysteresis or/and experimental error. In order to answer question 1. above we collated data for $T_{MIT}(n)$ starting from 1936 (see Table II). The limiting temperatures of the transitions either determined by hysteresis or by experimental error are plotted in Fig. 3 , by open circles for V_8O_{15} and by full circles for all other oxides. A straight line was fitted to the data points of each of the four groups of oxides (a') - (d'). The resulting equations and Patterson correlation coefficients (R^2) are shown below:

$$(a') T_{MIT} = 337.3(1 - 1.02/n)K \text{ for } 1/n = 1, 1/2, 1/4 \text{ and } 0, R^2 = 0.993$$

$$(b') T_{MIT} = 339.4(1 - 2.98/n)K \text{ for } 1/n = 1/5, 1/6, \text{ and } 0, R^2 = 0.997$$

$$(c') T_{MIT} = 316.5(7.09/n - 1)K \text{ for } 1/n = 1/3, 1/4, 1/5 \text{ and } 1/7, R^2 = 0.998$$

$$(d') T_{MIT} = 339.3(1 - 6.97/n)K \text{ for } 1/n = 1/7, 1/9 \text{ and } 0, R^2 = 0.999.$$

Lines (a) - (d) which represent the systematics are good approximations to the lines (a') - (d') fitted to the collected experimental data of the corresponding groups.

6. Figure Captions

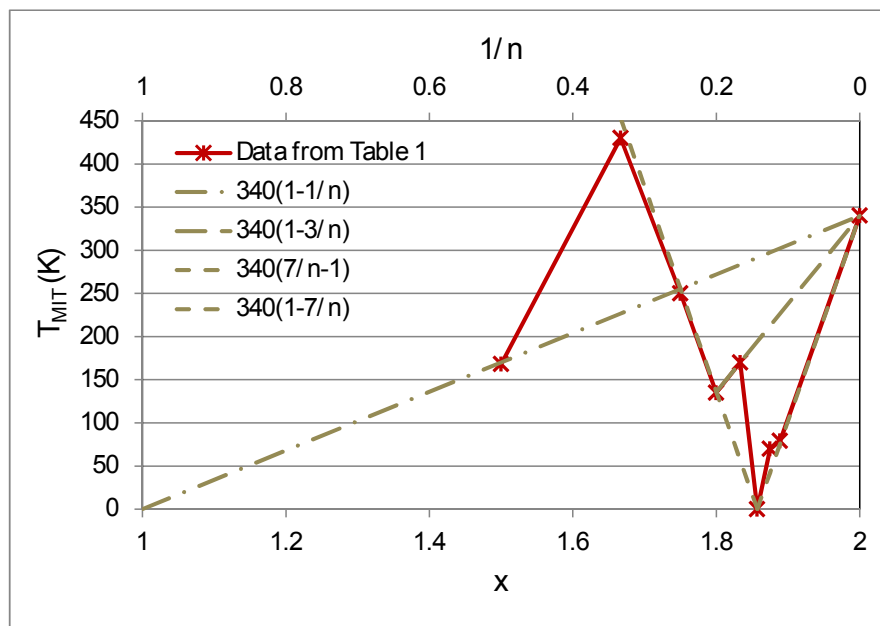


Fig. 1

Figure 1: T_{MIT} as function of x (primary horizontal axis) and $1/n$ (secondary horizontal axis). Symbols represent data from Table 1 connected by solid lines and dashed lines represent the systematics.

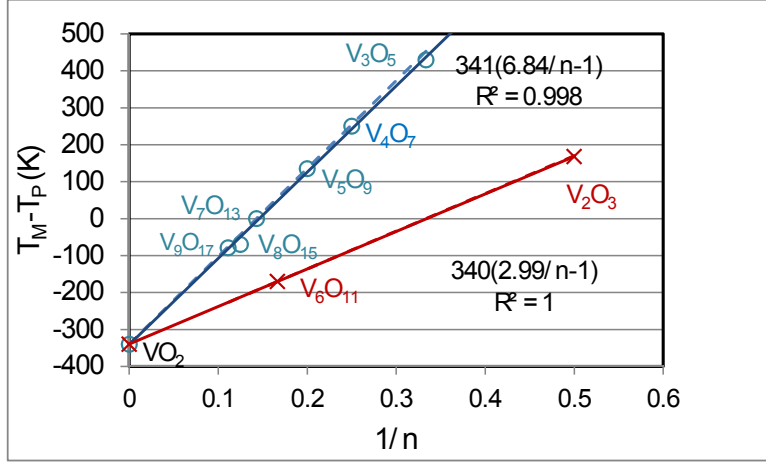


Fig. 2

Figure 2: $T_M - T_P$ as function of $1/n$. Symbols represent data points, solid lines represent linear trendlines fitted to the data and dashed lines represent the two simple expressions of $T_M - T_P$. Note that the lower dashed line is indistinguishable from the corresponding solid line.

Table 1: Vanadium oxides V_nO_{2n-1} (positive n) and their M-I transition temperatures (T_c)

n	V_nO_{2n-1}	T_{MIT} (K)	Reference
1	VO	metallic	[8]
2	V_2O_3	168	Table II in [6]
3	V_3O_5	430	[7]
4	V_4O_7	250	Table II in [6]
5	V_5O_9	135	Table II in [6]
6	V_6O_{11}	170	Table II in [6]
7	V_7O_{13}	metallic	[6]
8	V_8O_{15}	70	Table II in [6]
9	V_9O_{17}	79	[10]
∞	VO_2	340	Table II in [6]

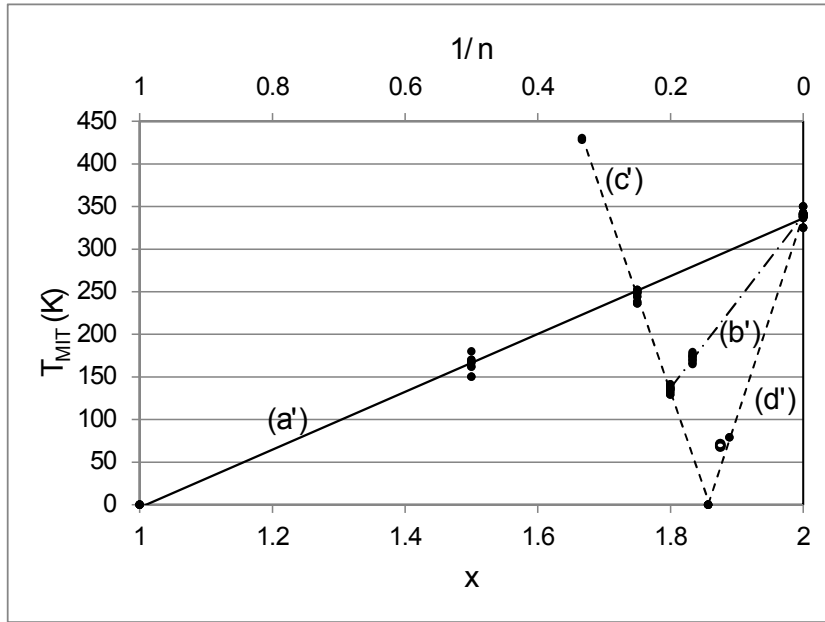


Fig. 3

Figure 3: T_{MIT} as function of x (primary horizontal axis) and $1/n$ (secondary horizontal axis). Symbols represent data from Table 2, straight lines are fitted linear trendlines to the (a') - (d') groups of data.

7. References

References

- [1] U. Schwingenschloegl and V. Eyert, *Ann. Phys. (Leipzig)* 13 (2004) 475.
- [2] J. M. Allred and R. J. Cava, *J. Solid State Chem.* 198 (2013) 10.
- [3] J. D. Budai, J. Hong, M. E. Manley, E. D. Specht, C. W. Li, J. Z. Tischler, D. L. Abernathy, A. H. Said, B. M. Leu, L. A. Boatner, R. J. McQueeney and O. Delaire, *Nature* 515 (2014) 535 and references therein.
- [4] K. Nagasawa, *Mater. Res. Bull.* 6 (1971) 853.
- [5] B. Fisher and J. Grunzweig-Genossar, *Solid State Commun.* 33 (1980) 965.
- [6] S. Kachi, K. Kosuge and H. Okinaka, *J. Solid State Chem.* 6 (1973) 258.
- [7] N. F. Kartenko, E. I. Terukov and F. A. Chudnovskii, *Sov. Phys. Solid State* 18 (1976) 1029.
- [8] F. Rivadulla, J. Fernandez-Rossier, M. Garcia-Hernandez, M. A. Lopez-Quintela, J. Rivas and J. B. Goodenough, *Phys. Rev. B* 76 (2007) 205110.
- [9] H. Kuwamoto, N. Otsuka, H. Sato, *J. Solid State Chem.* 36 (1981) 133.
- [10] S. Nagata, F. H. Keesom, H. Kuwamoto, N. Otsuka, N. Sato, *Phys. Rev. B* 23 (1981) 411.
- [11] A. Perucchi, L. Baldassarre, P. Postorino and S. Lupi, *J. Phys.: Condens. Matter* 21 (2009) 323202.
- [12] V. N. Andreev and V. A. Klimov, *Physics of the Solid State*, 53 (2011) 2424.
- [13] C. T. Anderson, *J. Amer. Chem Soc.* 58 (1936) 564.
- [14] M. Foex, *C. R. Acad. Sci.* 223 (1946) 1126.
- [15] F. J. Morin, *Phys. Rev. Lett.* 3 (1959) 34.

Table 2: Vanadium oxides V_nO_{2n-1} (positive n) and their M-I transition temperatures (T_c)

n	V_nO_{2n-1}	T_{MIT} (K)	Reference
1	VO	metallic	[8]
2	V_2O_3	170	[13]
2	V_2O_3	162 - 180	[14]
2	V_2O_3	153 - 165	[15]
2	V_2O_3	168 ± 2	[16]
2	V_2O_3	150 - 162	[17]
2	V_2O_3	168	[6]
2	V_2O_3	150 - 170	[19]
3	V_3O_5	430	[20]
3	V_3O_5	428	[12]
4	V_4O_7	250 ± 2	[16, 4]
4	V_4O_7	250, 244 - 250	[4, 6, 18]
4	V_4O_7	237 ± 1	[21]
5	V_5O_9	139 ± 2	[16]
5	V_5O_9	135 ± 3	[4]
5	V_5O_9	135, 129 - 135	[6, 18]
6	V_6O_{11}	177 ± 2	[16]
6	V_6O_{11}	170 ± 3	[4]
6	V_6O_{11}	170, 174 - 177	[4, 6, 18]
6	V_6O_{11}	165 - 170	[22]
7	V_7O_{13}	metallic	[16, 4, 6]
8	V_8O_{15}	70, 70 ± 1	[4, 6, 18]
8	V_8O_{15}	69 ± 1	[23]
9	V_9O_{17}	79	[9, 10]
∞	VO_2	325 - 350	[15]
∞	VO_2	338.5 ± 2	[24]
∞	VO_2	340 ± 2	[16, 25]
∞	VO_2	339 ± 1	[26]
∞	VO_2	340 ± 1	¹² [27]
∞	VO_2	340	[6]

- [16] K. Kosuge, J. Phys. Chem. Solids 28 (1967) 1613.
- [17] D. B. McWhan, A. Menth, J. P. Remeika, W. F. Brinkman and T. M. Rice, Phys. Rev. B 7 (1973) 1920.
- [18] J. M. Honig and L. L. Van Zandt, Annu. Rev. Mater Sci. 5 (1975) 225.
- [19] H. Kuwamoto, J. M. Honig, and J. Appel, Phys. Rev. B 22 (1980) 2626.
- [20] F. A. Chudnovskii, E. I. Terukov and D. I. Khomskii, Solid State Commun. 25 (1978) 573.
- [21] V. N. Andreev and V. A. Klimov, Physics of the Solid State, 51 (2009) 2235.
- [22] V. N. Andreev and V. A. Klimov, Physics of the Solid State, 55 (2013) 1829.
- [23] H. Ueda, K. Kitazawa, T. Matsumoto, H. Takagi, Solid State Commun. 125 (2003) 83.
- [24] H. Sasaki and A. Watanabe, J. Phys. Soc. Japan, 19 (1964) 1748.
- [25] R. F. Bongers, Solid State Commun, 3 (1965) 275.
- [26] L. A. Ladd and W. Paul, Solid State Commun, 7 (1969) 425.
- [27] J. B. MacChesney and H. J. Guggenheim, J. Phys. Chem. Solids, 30 (1969) 225.